Epitaxial Growth of GaN on (0001) Al_2O_3 Substrate

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The effect of growth parameters, such as the flow rate of HCl, the growth temperature and the distance of substrate from the outlet of NH_3, on the vapor phase epitaxy of GaN on (0001)Al_2O_3 substrate are investgated. The single crystal layer is grown on the substrate whose temperature is between 1010℃ and 1055℃. At the growth temperature outside of this range, the grown layers consist of polycrystalline GaN. The carrier concentration and electron mobility of the single crystals are $3\sim7\times10^{19}cm^{-3}$ and $50\sim60\ cm^2/V\cdot sec$, respectively. The surface patterns of grown single crystal layers depend mainly on the angle between the direction of the stream of NH_3 gas and the axis of the substrate in the growth region.

§ 1. Introduction

In recent years, a III-V compound semiconductor GaN has been investigated with large interest for the possibility of the blue light emitting material, and its photoluminescence (undoped GaN,[1-5] doqed GaN[6-10]) and electroluminescence[11-16] have been measured by many authors. Several growth techniques of GaN have been reported,[17-21] but the most widely used method, at the present time, for the preparation of single crystal is that of Maruska and Tiejen,[22] where a single crystal layer of GaN is grown on (0001) Al_2O_3 substrate using the reaction between GaCl and NH_3 vapors in the open tube system. However, the growth conditions used in the method are considerably different from author to author.[1-10,22-26] For example, the flow rate of HCl is in the range of a few-200 ml/min, and the growth temperature is in the range of 850-1150℃, depending on the workers. The growth rete of GaN on the substrate depends on these growth parameters, and it has been shown by Shintani and Minagawa[25] that the growth rate is proportional to the concentration of GaCl in the growth region.

This paper presents the experimental results on the effect of growth parameters, such as the flow rate of HCl, the growth temperature and the position of substrate, on the crystal quality of GaN layers grown on (0001)Al_2O_3 substrates. The crystal quality is investigated by X-ray Laue photograph technique and electrical properties. The relations between the growth morphology and the crystal quality are also reported.

§ 2. Experimental

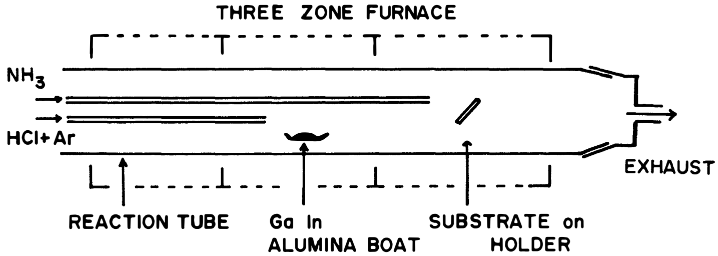

Fig. 1. Schematic diagram of the growth appratus. The length of the furnace is 1 m. The doping zone is used for pre-heating of gases in the present experiment.

The electric furnace used here consists of 3 zones as shown in Fig. 1. The left zone is for impurity doping, the middle a Ga source zone and the right a growth region, respectively. The doping zone is used merely for pre-heating of gases in the present experiments, and is held at about 650℃. The temperature of the growth region is essentially constant extending about 10 cm long, and is held at a setting temperature in an accuracy of ±2℃. The total length of the quartz reaction tube including outside of the furnace is 2 m and its inside diameter 30 mm. The inside diameters of the quartz pipes for HCl+Ar and NH_3 gases are both 6 mm. The HCl gas passing through the cold trap of dry ice is mixed with Ar carrier gas using an aspirator. The purites of gases are HCl(99.9%), NH_3 (99%) and Ar(99.999%), respectively. The Ga source in an alumina boat has a purity of 6-nine. The sapphire disk oriented (0001) plane with 0.5 mm thick and 20 mm diameter is cut in four pieces for substrate. A substrate is placed at an angle of 45° with respect to the horizontal axis on a quartz holder. The substrates are cleaned by water, acetone and trichlorätylen. Through the present experiments, the constant growth conditions are the flow rate of NH_3 1.25 l/min, the flow rate of Ar 1 l/min, the Ga source temperature 900℃. The standard growth time is 3 hr.

§ 3. Results and Discussions

3.1 Effect of HCl flow rate

Figure 2 shows the growth rate of GaN layer grown on (0001) Al_2O_3 substrate under the flow rate of HCl in the range of 1-8 ml/min, where the growth temperature is 1035 ℃ and the distance of substrate from the outlet of NH_3 2 cm. Another growth conditions are shown in the end of § 2. The growth rate increases almost linearly with increase in the flow rate of HCl. This dependence is similar to the results in refs. 25 and 26. But, in our case, the crystal quality depends on the flow rate of HCl. That is, when the rate is smaller than 2 ml/min, many pin-holes

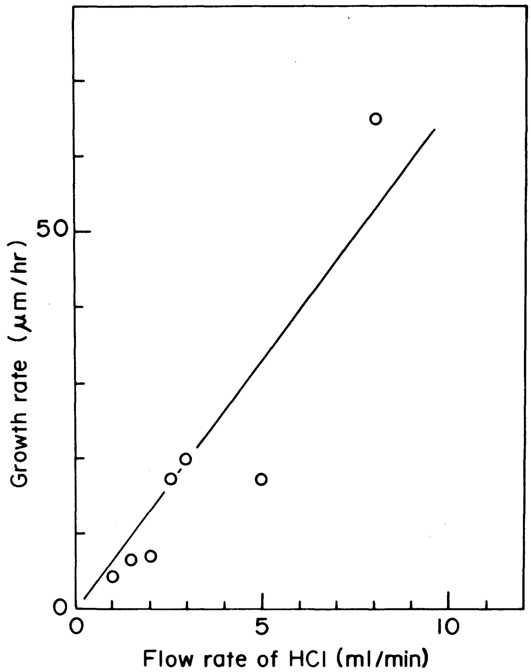

Fig. 2. The growth rate of GaN layer depending on the flow rate of HCI. The thickness of grown layer is measured at the center of substrate.

present on the surface, although the crystal is almost transparent. On the other hand, if it exceeds 3 ml/min, the crystal colour becomes black. Especially, if the flow rate is larger than 5 ml/min, the grown layers become to polycrystal and the colour is deep black.

3.2 Effect of substrate position

The relation between the thickness of GaN layer and the distance of substrate from the outlet of NH_3 under 3 hr growth run is shown in Fig. 3, where the flow rate of HCl is 3 ml/min and the growth temperature is 1030℃. When the distance exceeds about 6 cm, the layer does not grow uniformly. According to Shintani and Minagawa,[25] the growth rate of GaN depends on the GaCl concentration in the growth region, and the GaCl concentration decreases exponentialy with increasing the distance. So, the growth rate decreases also exponentialy with the distance. Figure 3 shows the similar result to them. But, when the distance is smaller than 1 cm, the single crystal layers can not be obtained.

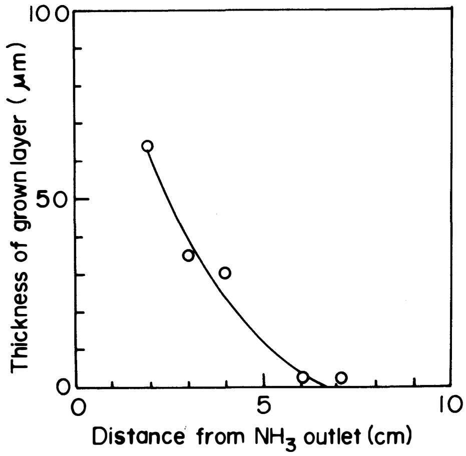

Fig. 3. The relation between the thickness of grown layer under 3 hr growth run and the distance of substrate from the outlet of NH_3.

3.3 Effect of growth temperature

The temperature dependence of the growth rate is shown in Fig. 4, where the growth rate increases monotonically with increase in growth temperature. The another growth parameters, in addition to the conditions in §2, are the flow rate of HCl 2.5 ml/min and the distance of substrate from the outlet of NH_3 1.5 cm. In Fig. 5, we present the surface patterns and the back-reflection X-ray Laue photographs of the crystals grown at each different temperature. The surface patterns are quite different for each temperature. The crystal layer grown at 890℃ shows irregular pattern, but the hexagonal patterns are clearly observed on the crystals grown at 1010 and 1035℃. A hexagon on the surface becomes larger and larger with the growth temperature up to 1055℃. However, it disappears again on the crystals grown at higher than 1065℃. The Laue photographs also change depending on the temperature. The diffract pattern of the crystal grown at 890℃ consists of some rings instead of spotts, and shows the layer consists of polycrystalline GaN. As the temperature is raised, the spots corresponding to hexagonal symmetry of (0001)plane

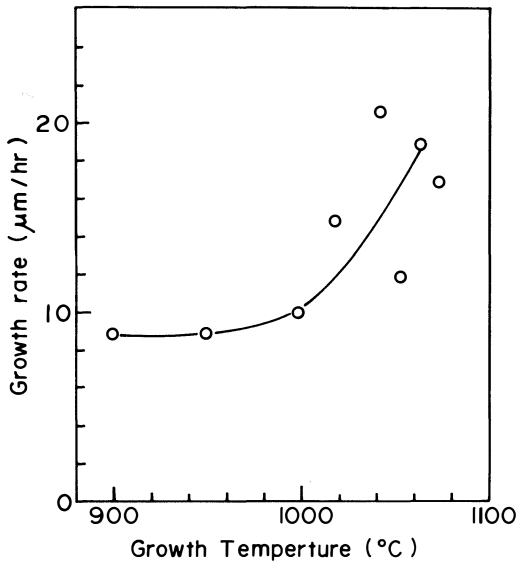

Fig. 4. The temperature dependence of the growth rate.

begin to appear, but the traces of rings are still remained at 990℃. The layers grown at 1010℃ and 1035℃ exhibit clear spots with hexagonal symmetry, and this Laue pattern does not change up to 1055℃. But, when the growth temperature exceeds 1065℃, the Laue photographs show again the ring patterns. From these observations, it is found that the crystals grown at temperatures in the range 1010-1055℃ are single crystal whose c-axis is coincident with the c-axis of the substrate. On the other hand, at lower than 990℃ and at higher than 1065℃, the surfaces of the layers become to irregular and the grown crystals consist of fiber structures rounding each other about c-axis. In conclusion, under our experimental conditions, the temperature range where the single crystal growth is possible is between 1010℃ and 1055℃. Furthermore, the surfaces of the layers grown at 1045℃ and 1055℃ are most smoothy and lustrous.

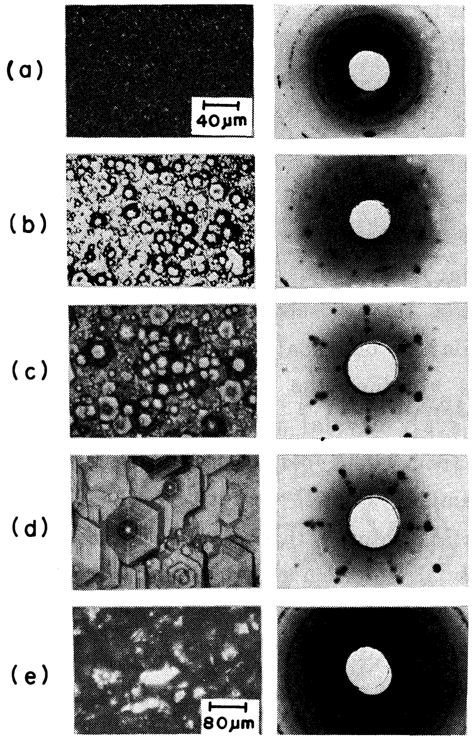

Fig. 5. The temperature dependences of the surface photographs(left) and the back-reflection X-ray Laue photographhs(right). The growth temperatures are (a)890℃, (b)990℃, (c)1010℃, (d)1035℃ and (e) 1075℃. The scales for surface photographs are all same to (a) except for (e).

According to Nishinaga and Mizutani,[27,28] in the case of the vapor phase heteroepitaxy, the temperature range where the good single crystal growth is possible becomes narrower with the increase in the misfit between each lattice constant. The misfit of the lattice constant along the a-axis in the (0001)plane between GaN and Al_2O_3 is about 33%.[29] So, this large misfit of lattice constant may be one of the reasons for the narrowness of the temperature range of the single crystal growth. But, the single crystal growth at lower[1] than 1010℃ and at higher[23] than 1055℃ have also been reported. So, the temperature range of the single crystal growth should be affected not only by the degree of the misfit of the lattice constant but also by the another growth conditions.

The electron mobility and the electron concentration of these crystals at room temperature are as follows. The mobilities of the crystals grown at 890℃ and at higher than 1065℃ are 3~15 $cm^2/V\cdot sec$, which are clearly smaller than the values of 50~60 $cm^2/V\cdot sec$ for the crystals grown at the temperatures in the range 990-1055℃. The carrier concentrations are abut $3\sim7\times10^{19}$ cm^{-3} for all crystals except the crystals grown at 890℃ whose carrier concentrations exceed 10^{20} $cm.^{-3}$

3.4 Growth morphology and crystal orientation

The single crystal layers grown on (0001)Al_2O_3 substrate exhibit mainly three types of surface pattern as illustrated by Fig. 6, where (a) shows the pyramidal surface of hexagonal symmetry, (b) the scrollwork aspect and (c) the scaly growth structure. These growth morphologies have also been reported in the literature.[23,24] Ilegems[24] have observed that the pyramidal structure was seen on the crystals grown on substrates placed far downstream from the $GaCl:NH_3$ mixing zone, and as the substrates came near to the mixing zone, the grown layers began to have a flat or conical aspect and a surface similar to our scaly pattern. Wickenden et al.[23] have obtained the stepped crystal similar to our scaly crystal using the substrate oriented 10° from (0001)plane. In our experiments, the pyramidal surface pattern is observed on the crystals thinner than 10 μm, and the scrollwork appears on the crystals thicker than 30 μm. The scaly pattern does not depend on the thickness. The grown layers showing these three patterns are all single crystals, and the cross sections are similar to Fig. 7, which is the electron microscope photograph of the cross section of a scaly crystal.

Comparing the positions of the Laue spotts of grown layer with those of substrate, it is found that the c-axis of the scaly crystal shows the off-axis of about 2～7°, depending on samples, from the c-axis of substrate. On the other hand, the c-axes of the scrollwork and pyramidal crystals coincide with the c-axis of substrate. The correctness of the c-axis of substrate used in the present experiments is about ± 0.1°.

Figure 8 shows the surface photograph and its illustration of a sample whose thickness changes depending on the position. In this sample, the pyramidal pattern appears in the thin layer region, and the scrollwork aspect is observed in the region with thicker layer. This result may show that the pyramidal surface pattern of thin layer changes into the scrollwork pattern with increase in the thickness of grown layer.

Figure 9 shows three different methods of

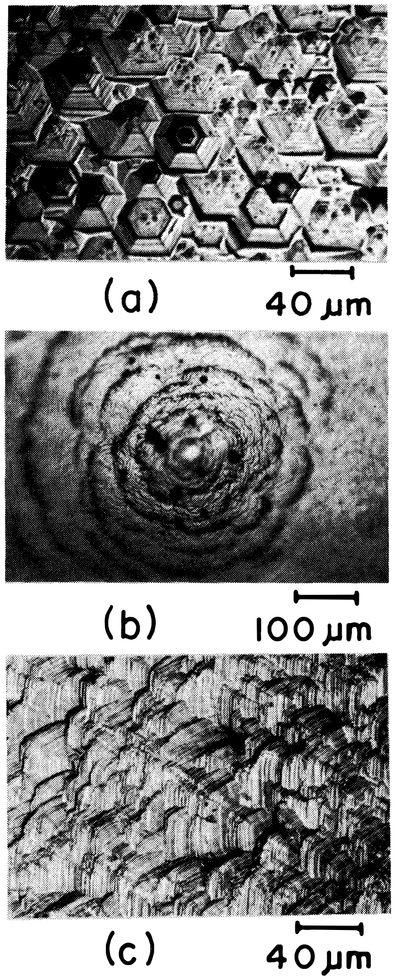

Fig. 6. The surface patterns of single crystal layers: (a) the pyramidal, (b) the scrollwork and (c) the scaly.

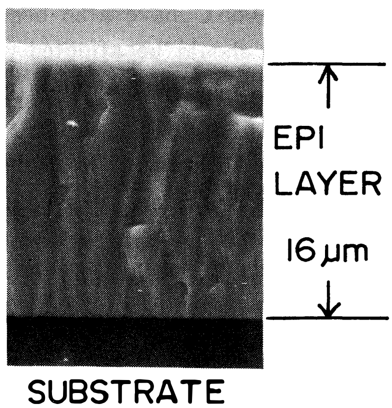

Fig. 7. The electron microscope photograph of the cross section of the crystal with scaly pattern. All single crystal layers exhibit the cross sections similar to this.

the vapor epitaxy used for checking the reason of the off-axis of the c-axis of scaly crystals. In the case of (a), the quartz block is placed after substrate and the substrate is horizontally, The method of (b) is used in the preceeding experiments. The substrate, in the case of (c), is placed also horizontally without quartz block. The direction of NH_3 gas stream mixed with GaCl in each method may be thought to be as shown in the figure. For the case of (a) and (b), the stream of $GaCl:NH_3$ mixing gas may be almost perpendicular to the substrate. Most of crystals grown by the methods of (a) and (b), show pyramidal pattern on the layer with thickness as thin as $\sim 10\,\mu m$, and exhibit scrollwork structure when the layer is thicker than $\sim 30\,\mu m$. On the other hand, the crystals grown by the method of (c) yield mainly scaly pattern. From these results, the reason of the off-axis of scaly crystal may be attributed to the direction of the stream of $GaCl:NH_3$ mixing gas with respect to the substrate.

The mobility of the scrollwork crystal is larger by a factor 1.5～2 than that of the scaly crystal. But, the difference of the carrier concentration is not observed between these patterns.

§4. Conclusion

The effect of various growth parameters on the vapor phase exitaxial growth of GaN on (0001)Al_2O_3 substrate has been investigated. The temperature range for single crystal growth is between 1010℃. and 1055℃ The crystals grown at temperatures outside of this range consist of polycrystalline fiber structure. The surface patterns of single crystal layers change mainly depending on the angle between the

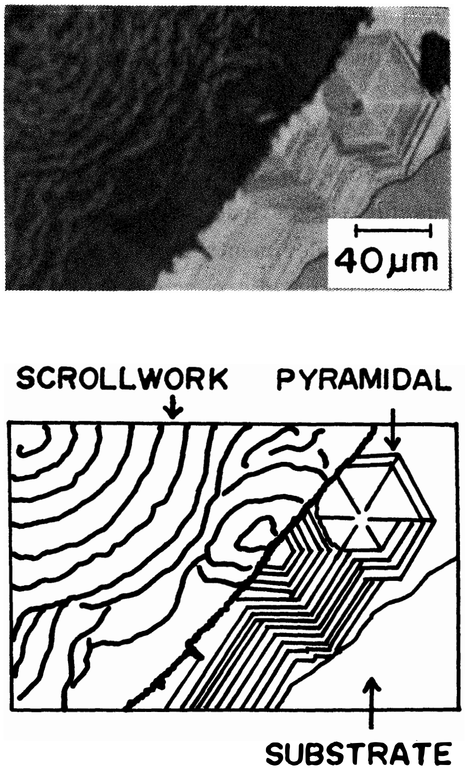

Fig. 8. The photograph (upper) and its illustration (lower) of a sample including both pyramidal and scrollwork patterns. The layer of pyramidal part is thinner than that of scrollwork part.

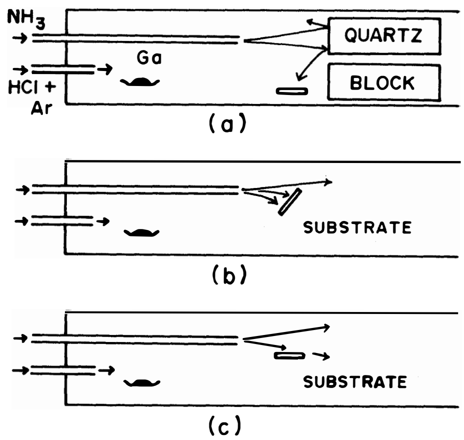

Fig. 9. The three growth methods for checking the relation between the surface patterns and the direction of NH_3 gas stream mixed with GaCl. In the methods of (a) and (b), the grown single crystals have pyramidal surface for thin layers and have scrollwork aspect for thick layers. In the case of (c), the layers with scaly surface pattern are grown.

direction of the stream of NH_3 gas and the c-axis of substrate in the growth region. They depend also on the thickness of grown layers.

Acknowledgments

The authors would like to express sincere thanks to Prof. M. Aoki of Tokyo Univ. for useful suggestions in the crystal growth of GaN, and to thank Mr. S. Tachi for his initial experiments in this work. They would also like to thank Mr. N. Nakatani for the electron micro-scope photographs of GaN layer.

References

1) J. I. Pankove, H. P. Maruska and J. E. Berkeyheiser: *Proc. Intern. Conf. Physics Semiconductors, Elsevier, 1972*, ed. M. Miasek (Elsevier Pub. Comp., Warsaw, 1972) p. 593.
2) R. Dingle, D. D. Sell, S. E. Stokowski and M. Ilegems: Phys. Rev. **B4** (1971) 1211.
3) B. Monemer: Phys. Rev. **B10**(1974) 676.
4) T. Matsumoto and M. Aoki: Japan. J. Appl. Phys. **13**(1974) 1804.
5) J. M. Hvam and E. Ejder: J. Luminescence **12, 13**(1976) 611.
6) M. Ilegems, R. Dingle and R. A. Logan: J. Appl. Phys. **43**(1972) 3797.
7) T. Matsumoto, M. Sano and M. Aoki: Japan. J. Appl. Phys. **13**(1974) 373.
8) M. Ilegems and R. Dingle: J. Appl. Phys. **43**(1973) 4234.
9) O. Lagerstedt and B. Monemar: J. Appl. Phys. **45**(1974) 2266.
10) J. I. Pankove, J. E. Berkeyheiser and E. A. Miller: J. Appl. Phys. **45**(1974) 1280.
11) J. I. Pankove, E. A. Miller, D. Richman and J. E. Berkeyheiser: J. Luminescence **4** (1971) 63.
12) H. P. Maruska, D. A. Stevenson and J. I. Pankove: Appl. Phys. Letters **22**(1973) 303.
13) J. I. Pankove: J. Luminescence **7**(1973) 114.
14) J. I. Pankove, M. T. Duffy, E. A. Miller and J. E. Berkeyheiser: J. Luminescence **8** (1973) 89.
15) J. I. Pankove: IEEE Trans. Electron-Devices **ED-22**(1975) 721.
16) J. Jacob and D. Bois: J. Appl. Phys. **30**(1977) 412.
17) R. A. Logan and C. D. Thurmond: J. Electrochem. Soc. **119**(1972) 1727.
18) T. L. Chu: J. Electrochem. Soc. **118**(1971) 1200.
19) H. J. Hovel and J. J. Cuomo: Appl. Phys. Letters **20**(1972) 71.
20) K. R. Faukner, D. K. Wickenden, B. J. Isherwood, B. P. Richard and I. H. Scobey: J. M Mater. Sci. **5**(1970) 308.
21) R. B. Zetterstrom: J. Mater. Sci. **119**(1972) 761.
22) H. P. Maruska and J. J. Tiejen: Appl. Phys. Letters **15**(1969) 327.
23) D. K. Wickenden, K. R. Faukner and R. W. Brander: J. Cryst. Growth **9**(1971) 158.
24) M. Ilegems: J. Cryst. Growth **13, 14**(1972) 360.
25) A. Shintani and S. Minagawa: J. Cryst. Growth **22**(1974) 1.
26) M. Sano and M. Aoki: Japan. J. Appl. Phys. **15**(1976) 1943.

27) T. Nishinaga and T. Mizutani: Japan. J. Appl. Phys. **14**(1975) 753.
28) T. Nishinaga: *Oyo Butsuri* **45**(1976) 891 (in Japanese).
29) B. B. Kosicki and D. Kahng: J. Vacuum Sci. Techol. **6**(1969) 593.

(Received October 31, 1978)